

What is claimed is:

1. In a method of conducting a heterogeneous chemical reaction including the steps of forming a reactant mixture comprising one or more heterogeneous reactant(s) in a reactor, and causing said reactant(s) to react in the presence of a solid catalyst under near- or supercritical reaction conditions to yield a reaction mixture, the improvement which comprises using as said solid catalyst a macroporous solid catalyst having a surface area of from about 50-400 m<sup>2</sup>/g.

2. The method of claim 1, said surface area being about 200 m<sup>2</sup>/g.

3. The method of claim 1, said catalyst comprising a perfluorinated polymer having sulfonic acid groups coupled thereto.

4. The method of claim 1, said chemical reaction selected from the group consisting of alkylation, acylation, isomerization, aromatic disproportionation, alcohol synthesis and Fischer-Tropsch reactions.

5. The method of claim 4, said chemical reaction being an alkylation reaction wherein said reactants include an isoparaffin, an olefin, and a molar excess of an inert co-solvent or diluent.

6. The method of claim 5, said isoparaffin selected from the group consisting of C<sub>4</sub>-C<sub>10</sub> isoparaffins, and said olefin selected from the group consisting of the C<sub>2</sub>-C<sub>10</sub> olefins.

7. The method of claim 5, said co-solvent or diluent having a critical temperature less than the critical temperatures of each of said isoparaffin and olefin.

8. The method of claim 5, said co-solvent or diluent selected from the group consisting of carbon dioxide, methane, ethane, hydrogen, and mixtures thereof.

9. The method of claim 1, said reaction being carried out at a temperature of from about 0.9-1.3 T<sub>c</sub> of the reactant mixture.

10 5 10. The method of claim 9, said temperature being from about 1.01-1.2 T<sub>c</sub> of the reactant mixture.

11. The method of claim 1, said reaction being carried out at a pressure of from about 0.9-2.5 P<sub>c</sub> of the reactant mixture.

12. The method of claim 11, said reaction being carried out at a pressure of from about 1.01-1.2 P<sub>c</sub> of the reactant mixture.

13. The method of claim 1, said reactant mixture being formed by continuously introducing said reactant(s) into said reactor including a co-solvent or diluent under substantially steady state reactor conditions, said catalyst being susceptible to deactivation owing to coke laydown during the course of said reaction, said method including the step of regenerating said catalyst by terminating said introduction of at least one of said reactant(s) prior to a time when said solid catalyst is significantly deactivated owing to coke laydown, elevating the pressure and/or lowering the temperature within said reactor to remove at least a portion of any coke on the catalyst, resuming introduction of said reactant(s) into said reactor and reestablishing said substantially steady state conditions.

14. The method of claim 13, the pressure within said reactor being elevated by at least about 40%, as compared with the pressure within the reactor during said chemical reaction.

25 15. The method of claim 13, the reactor temperature being lowered while still maintaining the reactor temperature above the T<sub>c</sub> of the co-solvent or diluent.

16. A method of conducting a heterogeneous chemical reaction comprising the steps of:

introducing one or more heterogeneous reactant(s) and a co-solvent or diluent into a reactor to form a reactant mixture, and causing said reactant(s) to react therein to yield a reaction mixture in the presence of a solid catalyst susceptible to deactivation owing to coke laydown during the course of said reaction,  
5 said reaction being carried out under substantially steady state near- or supercritical reaction conditions for the reactant mixture;

regenerating said catalyst of coke during the course of said reaction, including the steps  
10 of interrupting said chemical reaction by terminating said introduction of at least one of said reactant(s) into said reactor prior to a time when the catalyst is significantly deactivated, and regenerating said catalyst by elevating the pressure within said reactor and/or lowering the reactor temperature to effect at least partial removal of coke from said catalyst; and  
15 resuming said chemical reaction by again introducing said reactant(s) into the reactor, and reestablishing said substantially steady state conditions.

17. The method of claim 16, said regenerating step being carried out before the rate of production of a desired reaction product falls by a factor of 20%, as compared with  
20 the steady state reaction product production rate prior to the regenerating step.

18. The method of claim 16, said solid catalyst having a surface area of from about 50-400 m<sup>2</sup>/g.

25 19. The method of claim 16, said catalyst comprising a perfluorinated polymer having sulfonic acid groups coupled thereto.

20. The method of claim 16, said chemical reaction selected from the group consisting of alkylation, acylation, isomerization, aromatic disproportionation, alcohol synthesis  
30 and Fischer-Tropsch reactions.

21. The method of claim 20, said chemical reaction being an alkylation reaction wherein said reactants include an isoparaffin, an olefin, and a molar excess of an inert co-solvent or diluent.

5 22. The method of claim 21, said isoparaffin selected from the group consisting of C<sub>4</sub>-C<sub>10</sub> isoparaffins, and said olefin selected from the group consisting of the C<sub>2</sub>-C<sub>10</sub> olefins.

10 23. The method of claim 21, said co-solvent or diluent having a critical temperature less than the critical temperatures of each of said isoparaffin and olefin.

15 24. The method of claim 21, said co-solvent or diluent selected from the group consisting of carbon dioxide, methane, ethane, hydrogen, and mixtures thereof.

20 25. The method of claim 16, said reaction being carried out at a temperature of from about 0.9-1.3 T<sub>c</sub> of the reactant mixture.

26. The method of claim 25, said temperature being from about 1.01-1.2 T<sub>c</sub> of the reactant mixture.

20 27. The method of claim 16, said reaction being carried out at a pressure of from about 0.9-2.5 P<sub>c</sub> of the reactant mixture.

25 28. The method of claim 27, said reaction being carried out at a pressure of from about 1.01-1.2 P<sub>c</sub> of the reactant mixture.

30 29. The method of claim 16, the pressure within said reactor during said regenerating step being elevated by at least about 40%, as compared with the pressure within the reactor during said chemical reaction.

30. The method of claim 16, the reactor temperature being lowered while still maintaining the reactor temperature above the  $T_c$  of the co-solvent or diluent.

31. The method of claim 16, including the step of recovering said removed  
5 coke.

32. An alkylation method comprising the steps of:  
providing a reactant mixture comprising a  $C_4$ - $C_{10}$  isoparaffin, a  $C_2$ - $C_{10}$  olefin, and a molar excess of carbon dioxide; and  
contacting said reactant mixture with a solid alkylation catalyst to produce a reaction mixture containing alkylate, said solid catalyst having a surface area of from about  $50$ - $400\text{m}^2/\text{g}$ ,  
said contacting step being carried out at a temperature of from about  $0.9$ - $1.3\text{ }T_c$  of the reaction mixture and at a pressure of from about  $0.9$ - $2.5\text{ }P_c$  of the reactant mixture.

33. The method of claim 32, said temperature being from about  $1.01$ - $1.2\text{ }T_c$  and said pressure being from about  $1.01$ - $1.2\text{ }P_c$ .

20 34. The method of claim 32, said catalyst comprising a perfluorinated polymer having sulfonic acid groups coupled thereto.

35. The method of claim 32, said reaction mixture having a fluid density of from about  $0.05$ - $0.65\text{ g/cc}$ .

25 36. The method of claim 32, said pressure being from about  $500$ - $3,000\text{ psi}$ .

37. The method of claim 32, said surface area being about  $200\text{ m}^2/\text{g}$ .

PROVISIONAL  
10  
15  
20  
25  
30  
35  
40  
45  
50  
55  
60  
65  
70  
75  
80  
85  
90  
95

38. The method of claim 32, said isoparaffin being selected from the group consisting of the C<sub>4</sub>-C<sub>5</sub> isoparaffins, and said olefin being selected from the group consisting of the C<sub>3</sub>-C<sub>6</sub> olefins.

5

39. The method of claim 38, said olefin being butene.

40. The method of claim 32, said reactant mixture having a peroxide content of up to 200 ppm.

10

41. The method of claim 32, said method being a continuous method wherein said isoparaffin and olefin are continuously directed to a reactor to form said reactant mixture therein, and the reactant mixture is reacted under substantially steady state conditions, said method further including the step of regenerating said catalyst of coke during said alkylation reaction, comprising the steps of interrupting said alkylation reaction by terminating said introduction of said isoparaffin and olefin to the reactor prior to a time when the catalyst is significantly deactivated, and elevating the pressure and/or lowering the temperature within said reactor to effect at least partial removal of coke from said catalyst, and thereafter resuming said alkylation reaction by again introducing said isoparaffin and olefin to the reactor, and reestablishing said substantially steady state conditions.

15

20

42. The method of claim 41, said regenerating step being carried out periodically during the course of said continuous method.

25

43. The method of claim 41, said reactor pressure being elevated during said regenerating step by at least about 40%, as compared with the pressure within the reactor during the alkylation reaction.

30

44. The method of claim 41, said regenerating step being carried out before the rate of production of a desired reaction product falls by a factor of 20%, as compared with the steady state reaction product production rate prior to the regenerating step.

100-200-300-400-500-600-700-800-900

45. The method of claim 41, including the step of establishing in said reactor a reaction pressure of from about 500-3000 psi during the course of said alkylation reaction.

46. The method of claim 41, the reactor temperature being lowered while still  
5 maintaining the reactor temperature above the Tc of the co-solvent or diluent.

47. The method of claim 41, including the step of recovering said removed coke.